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(54) Title: ROOM TEMPERATURE CURABLE OIL RESISTANT ELASTOMER COATING

(57) Abstract: The coating composition of the invention cures at room temperature, and forms a coating which is resistant to flex-fatigue, corrosive materials, environmental temperature variability and provides for excellent adhesion to flexible elastomeric substrates. The coating comprises (A) a hydrogenated acrylonitrile-butadiene copolymer, (HNBR) (B) a phenolic resin, (C) a di-or polyisocyanate, (D) a curing component, and (E) a solvent.

ROOM TEMPERATURE CURABLE OIL RESISTANT ELASTOMER COATING

FIELD OF THE INVENTION

[0001] The present invention relates to protective coatings on elastomers.

BACKGROUND OF THE INVENTION

[0002] Elastomeric materials are utilized in numerous industrial applications. For example, elastomeric materials are utilized in the manufacture of various hoses, seals, and insulating devices found in the engines of automobiles and other vehicles. In addition, devices for mounting the engines within these vehicles typically comprise one or more metal parts adhesively bonded to one or more elastomeric parts. In these and many other industrial applications utilizing elastomeric materials, the elastomeric materials are typically exposed to corrosive and degrading materials such as various solvents, oils and fuels. Elastomeric materials have a tendency to degrade when exposed to these types of materials, and there is a continuing search within the elastomer industry to create an elastomer which is resistant to corrosive materials.

[0003] One method of rendering elastomeric materials resistant to corrosive materials is to apply a protective coating to the elastomeric material. Various corrosion-resistant coatings previously utilized for both flexible substrates (e.g., elastomeric substrates) and rigid substrates (e.g., steel, stainless steel, aluminum or plastic) include polyurethanes, polysulfides and fluorocarbon elastomers. When applied to rigid substrates, traditional corrosion-resistant coatings such as fluorocarbon elastomers have been found to provide excellent resistance to oil and fuel. However, when applied to flexible elastomeric substrates such as natural rubber or polybutadiene, the fluorocarbon elastomers suffer from poor fatigue resistance, poor low temperature characteristics, and poor adhesion to the natural rubber or polybutadiene substrate.

[0004] U.S. Pat. No 4,774,288 discloses a hydrogenated copolymer of a conjugated diene and an α,β--unsaturated nitrile containing an active phenol-formaldehyde resin vulcanization system. The disclosure is directed to the bulk vulcanizate, which is characterized as having good compression set properties and a good resistance to oils

and good resistance to oxidative attack in air at elevated temperature aging under oxidizing conditions, however no mention is made suggesting that solvent borne coatings could be formed on flexible elastomeric substrates such as natural rubber and polybutadiene which might provide useful properties.

[0005] U.S. Patent 5,314,955 discloses a coating composition consisting of (a) a hydrogenated acrylonitrile-butadiene copolymer, (b) a phenolic resin, (c) a curing component, and (d) a solvent. This coating solves many of the problems of adhesion to rubber substrates combined with fatigue resistance and fuel resistance. One of the drawbacks of this coating composition is that it requires a high temperature bake to cure the coating and to promote adhesion to adjacent metal surfaces. Some parts such as helicopter rotor bearings are damaged by the high temperature bake. The high temperature bake is also costly in production since it adds a time delay and additional handling of the parts. There still exists a need for improved protective coatings for flexible elastomeric substrates such as natural rubber and polybutadiene that can be applied without additional high temperature exposure, but provide long-term flexibility, fatigue resistance over a broad service temperature range, and that exhibit effective adhesion to the substrate.

SUMMARY OF THE INVENTION

[0006] The coating composition of the invention is resistant to fatigue and temperature variability and provides for excellent adhesion to flexible elastomeric substrates and it cures at room temperature. More specifically, the coating composition of the invention comprises (A) a hydrogenated acrylonitrile-butadiene copolymer, (HNBR) (B) a phenolic resin, (C) a di-or polyisocyanate, (D) a curing component, and (E) a solvent. The present invention provides coatings having excellent adhesion to the elastomer substrate, resistance to corrosive materials and resistance to fatigue over a wide temperature range.

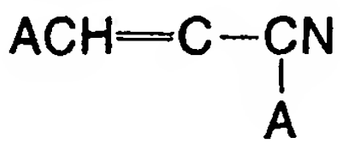
What is claimed is:

1. A coating composition comprising 5 to 30 weight percent of solids, said solids comprising (a) a hydrogenated copolymer of a conjugated diene and an unsaturated nitrile, (b) a phenolic resin, (c) a di- or polyisocyanate, (d) a curing component, and (e) from 70 to 95% of a solvent.

2. A coating composition according to claim 1 wherein the conjugated diene is selected from the group consisting of 1,3-butadiene; 2,3-dimethylbutadiene; 1,3-pentadiene; 1,3-hexadiene; 2,4-hexadiene; 1,3-heptadiene; piperylene; and isoprene.

3. A coating composition according to claim 2 wherein the conjugated diene is 1,3-butadiene.

4. A coating composition according to claim 1 wherein the unsaturated nitrile corresponds to the following formula:



wherein each A is hydrogen or a hydrocarbyl group having from 1 to about 10 carbon atoms.

5. A coating composition according to claim 1 wherein the unsaturated nitrile is acrylonitrile or methacrylonitrile.

6. A coating composition according to claim 1 wherein the hydrogenated copolymer has an unsaturation level between about 0.1 and 20 mole percent.

7. A coating composition according to claim 6 wherein the unsaturation level is between about 3 and 7 mole percent.

8. A coating composition according to claim 1 wherein the phenolic resin is prepared by reacting a phenolic compound with an aldehyde compound under acidic, neutral or basic conditions with an appropriate catalyst.

9. A coating composition according to claim 8 wherein the phenolic compound is selected from the group consisting of phenol, p-t-butylphenol, p-phenylphenol, m-bromophenol, o-chlorophenol, p-chlorophenol, p-alkoxyphenol, o-cresol, m-cresol, p-cresol, 2-ethylphenol, amylphenol, nonylphenol, xylenol, naphthol, carvacrol, cashew nutshell liquid, resorcinol, orcinol, phloroglucinol, pyrocatechol, pyrogallol, salicylic acid, bisphenol A, bisphenol S, and combinations thereof.

10. A coating composition according to claim 9 wherein the phenolic compound is phenol.

11. A coating composition according to claim 8 wherein the aldehyde compound is selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, 2-ethylbutrylaldehyde, 2-methylpentaldehyde, 2-ethylhexaldehyde, para-formaldehyde, trioxane, furfural, hexamethylenetetramine, and benzaldehyde.

12. A coating composition according to claim 11 wherein the aldehyde compound is formaldehyde.

13. A coating composition according to claim 1 wherein the curing component comprises elemental sulfur in combination with an organic accelerator.

14. A coating composition according to claim 13 wherein the organic accelerator is a derivative of a dithocarbamic acid, a xanthogenic acid, or a thiuram sulfide.

15. A coating composition according to claim 13 wherein the organic accelerator is selected from the group consisting of zinc dimethyldithiocarbamate, benzothiazyl disulfide, zinc isopropyl xanthate, N-pentamethylene-ammonium-N'-pentamethylenedithiocarbamate, and combinations thereof.

16. A coating composition according to claim 15 wherein the organic accelerator is a combination of zinc dimethyldithiocarbamate and benzothiazyl disulfide.

17. A coating composition according to claim 1 wherein the solvent is selected from the group consisting of ketones; acetates; toluene, xylene and their derivatives; nitropropane; and ethylene dichloride.

18. A coating composition according to claim 1 wherein the phenolic resin is present in an amount ranging from about 3 to 50 percent by weight of the hydrogenated copolymer and the curing component is present in an amount ranging from about 0.1 to 12 percent by weight of the hydrogenated copolymer.

19. A coating composition according to claim 18 wherein the phenolic resin is present in an amount ranging from about 5 to 15 percent by weight of the hydrogenated copolymer, the curing component is present in an amount ranging from about 1 to 6 percent by weight of the hydrogenated copolymer, and wherein the coating composition has a total solids content ranging from about 13 to 18 percent.

20. The coating composition of claim 1 wherein said di- or polyisocyanates is selected from the group consisting of as 1,6-hexamethylene diisocyanate;1,8-octamethylene diisocyanate;1,12-dodecamethylene diisocyanate;2,2,4-trimethylhexamethylene diisocyanate, and the like; 3,3'-diisocyanatodipropyl ether; 3-isocyanatomethyl-3,5,5'-trimethylcyclodexyl isocyanate; hexamethylene diisocyanate; 4,4'-methylenebis(cyclohexyl isocyanate); cyclopentalene-1,3-diisocyanate;cyclodexylene-1,4,-diisocyanate; methyl 2,6-diisocyanatocaprolate; bis-(2-isocyanatoethyl)-fumarate; 4-methyl-1,3-diisocyanatocyclohexane; trans-vinylene diisocyanate; 4,4'-methylene-bis(cyclohexylisocyanate); methane diisocyanates; bis-(2-isocyanatoethyl) carbonate ; N,N',N"-tris-(6-isocyanatohexamethylene)biuret, toluene diisocyanates; xylene diisocyanates; dianisidine diisocyanate; 4,4'-diphenylmethane diisocyanate;1-ethoxy-2,4-diisocyanatobenzene;1-chloro-2,4-diisocyanatobenzene; bis(4-isocyanatophenyl)methane; tris(4-isocyanatophenyl)methane; naphthalene diisocyanate; 4,4'-biphenyl diisocyanate; m-phenylene diisocyanate; p-phenylene diisocyanate; 3,3'-dimethyl-4,4'-biphenyl diisocyanate; p-isocyanatobenzoyl isocyanate; tetrachloro-1,3-phenylene diisocyanate; 2,4-toluene diisocyanate,2,6-toluene diisocyanate, 4,4'-isocyanate,bis-

[isocyanatopheny] methane polymethylene poly(phenyl isocyanate), isophrone diisocyanate, mixtures thereof .

21. The coating of claim 1 wherein said di- or polyisocyanate is present at from 3 to 30 wt. parts per 100 wt. parts of said hydrogenated copolymer of a conjugated diene and an unsaturated nitrile.

22. The coating of claim 1 wherein said di- or polyisocyanate is present at from 8 to 15 wt. parts per 100 wt. parts of said hydrogenated copolymer of a conjugated diene and an unsaturated nitrile.

23. A method of coating a substrate comprising applying a coating composition to the surface of the substrate wherein the coating composition comprises the coating composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D115/00 C08G18/62 C08G18/40 C08J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 314 955 A (HALLADAY) 24 May 1994 (1994-05-24) the whole document ---	1-18
A	DATABASE WPI Week 7746 Derwent Publications Ltd., London, GB; AN 1977-81821y XP002231137 & JP 52 117950 A (MITSUBISHI ELECTRIC), 3 October 1977 (1977-10-03) abstract --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9429 Derwent Publications Ltd., London, GB; AN 1994-238886 XP002231138 & JP 06 172552 A (BANDO CHEM), 21 June 1994 (1994-06-21) abstract	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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